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TANTALUM SPUTTERING TARGET AND METHOD OF MANUFACTURE

FIELD OF THE INVENTION

5   This invention relates to a method and apparatus for producing high purity tantalum and the high purity tantalum so produced. In particular, the invention relates to production of high purity tantalum.

BACKGROUND OF THE INVENTION

        Tantalum is currently used extensively in the electronics industry which employs
10   tantalum in the manufacture of highly effective electronic capacitors. This is mainly attributed to the strong and stable dielectric properties of the oxide film on the anodized metal. Both wrought thin foils and powders are used to manufacture bulk capacitors. In addition, thin film capacitors for microcircuit applications are formed by anodization of tantalum films, which are normally produced by sputtering. Tantalum is also sputtered in
15   an Ar-N_2 ambient to form an ultra thin TaN layer which is used as a diffusion barrier between a Cu layer and a silicon substrate in new generation chips to ensure that the cross section of the interconnects can make use of the high conductivity properties of Cu. It is reported that the microstructure and stoichiometry of the TaN film are, unlike TiN, relatively insensitive to the deposition conditions. Therefore, TaN is considered a much
20   better diffusion barrier than TiN for chip manufacture using copper as metallization material. For these thin film applications in the microelectronics industry, high purity tantalum sputtering targets are needed.

        Most of the tantalum metal produced in the world today is derived from sodium reduction of potassium heptafluotantalate (K_2TaF_7). Processes which are not adapted
25   commercially to any significant extent include the reduction of tantalum oxide (Ta_2O_5) with metallic reductants such as calcium and aluminum, and non metallic reductants carbon and carbon nitrogen; the reduction of the tantalum pentachloride ($TaCl_5$) with magnesium, sodium or hydrogen; and the thermal dissociation of $TaCl_5$.

        Reduced tantalum is obtained either as powder, sponge or massive metal. It
30   invariably contains significant amounts of oxygen, as well as other impurities such as reductants and impurities that may be present in the starting tantalum compounds. For removal of impurities in tantalum, electron beam melting is often conducted. During electron beam melting, most of the metallic impurities and interstitial gases are vaporized because of their high vapor pressure at the melting point of tantalum (2996°C).
35   Essentially all elements, except niobium, tungsten, molybdenum, uranium and thorium can

1   be eliminated this way. While the metallic impurities and nitrogen are removed by direct
volatilization, the removal of oxygen takes place via mechanisms involving formation and
evaporation of carbon oxides, aluminum oxides, water, as well as suboxides of tantalum.
The purity can be further improved by repeated electron beam melting. Other refining

5   processes include vacuum arc melting, vacuum sintering, molten salt electrorefining and
tantalum iodide refining, with the iodide process being the most promising technique for
removing tungsten and molybdenum.

The above mentioned refining methods are not effective for removal of niobium
from tantalum. Since tantalum and niobium are closely associated with each other in

10   nature, the removal of niobium is critical to prepare very high pure tantalum. In practice,
their separation is conducted before reduction via methods such as solvent extraction,
chlorination and fractional crystallization.

The tantalum target manufacturing process includes forging ingot into billet, surface
machining billet, cutting billet into pieces, cold rolling the pieces into blanks, annealing

15   blanks, final finishing and bonding to backing plates.

SUMMARY OF THE INVENTION

In accordance with the present invention there is provided a method and apparatus
for producing high purity tantalum sputtering targets and the high purity tantalum so

20   produced.

The method comprises purifying potassium heptafloutantalate, K_2TaF_7, reducing the
purified K_2TaF_7 to produce tantalum powder, refining the tantalum by reacting with iodine
and finally electron beam melting the tantalum to form a high purity tantalum ingot.

The starting material is commercial K_2TaF_7 salt, made by dissolving tantalum ores

25   in hydrofluoric and sulfuric acid mixture, followed by filtration, solvent extraction using
methkylisobutylketone (MIBK) and crystallization of K_2TaF_7. This can be repeated several
times to lower the impurity levels, in particular the level of Nb.

Sodium reduction of purified K_2TaF_7 is conducted in a liquid liquid reduction retort
where K_2TaF_7 and diluents (KCl and NaCl) are heated to about 1000°C. Molten sodium

30   is then injected into the retort for reacting with K_2TaF_7. Agitation of the reactants is
provided to accelerate the reduction reaction. After cooling, the mass is taken out of the
retort, crushed, leached and washed to separate tantalum powder from the salt mixture.

Tantalum refining is done by the iodide process or electron beam melting. These
methods can be used in parallel or in series. Electron beam melting is preferred as the last

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1 step because it results in an ingot which is suitable for further physical metallurgical steps toward the goal of target manufacture.

Electron beam melted ingot is forged into billets and surface machined. After surface machining, the forged billet is cut into pieces, which are further cold rolled into

5 blanks. Blank annealing is carried out in an inert atmosphere to obtain a recrystallized microstructure. The blanks are then machined to obtain a final finish and bonded to copper or aluminum backing plates.

For characterization of targets produced by the invented process, chemical analyses are conducted. The methods of chemical analysis used to derive the chemical descriptions

10 set forth herein are the methods known as glow discharge mass spectroscopy (GDMS) for metallic elements and LECO gas analyzer for non metallic elements.

The highly purified tantalum material of the present invention has less than 500 ppm by weight, total metallic impurities, an oxygen content of less than about 100 ppm, by weight, a molybdenum or tungsten content of not more than 50 ppm, by weight, and a

15 uranium and thorium content of not more than 10 ppb, by weight. It is also possible to produce tantalum having less than 5 ppm, by weight, total of molybdenum and tungsten.

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1   BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic diagram of the liquid liquid reaction retort used for sodium reduction of K_2TaF_7;

Figure 2 is a schematic diagram of an iodide cell;

5   Figure 3 is a schematic diagram illustration an iodide cell with a distillation unit;

Figure 4A and 4B are schematic diagrams of a tantalum target; and

Figure 5 is a graph of conductance of tantalum bar as a function of time.

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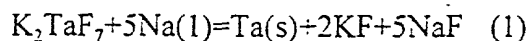
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1   DETAILED DESCRIPTION

1)   Precursor Purification and Sodium Reduction

In nature, tantalum generally occurs in close association with niobium, tin and other elements. The minerals most commonly used as raw materials in tantalum production are

5   Tantalite, Wodginite, Micolite and Samarskite. These minerals are enriched by wet gravity, magnetic or electrostatic methods. The concentrates are dissolved in a mixture of hydrofluoric and sulfuric acid. The resulting solution is filtered, then separated from niobium and other impurities in a solvent extraction plant. The tantalum concentrate is transferred into an aqueous solution and precipitated with ammonia to yield tantalum acid

10   ($Ta_2O_5xH_2O$), calcined at an elevated temperature to yield tantalum oxide. Alternatively, the tantalum is crystallized to potassium heptafloutantalate, by addition of KF and KCl to the hot aqueous solution obtained from solvent extraction. Impure potassium heptafloutantalate obtained by these methods must be further purified for use as a source of tantalum for the electronics industry.

15   In general, potassium heptafloutantalate may be purified by a procedure such as follows:

Technical grade potassium heptafloutantalate (K_2TaF_7) is dissolved in HF, e.g. a 49% HF solution. A mixture of HF and H_2SO_4 can also can also be used for the dissolution process. The amount of K_2TaF_7 dissolved depends on the temperature and

20   concentration of HF. Since the dissolution rate is very slow at room temperature, the mixture is heated e.g. to 90°C in a suitable container. The solution containing K_2TaF_7 is covered, to prevent losses due to evaporation, and stirred continuously. Time to dissolution is approximately one hour. A 65°C KCl solution is added to the K_2TaF_7 solution and the resulting solution is stirred while cooling to room temperature. The

25   tantalum in solution precipitates as K_2TaF_7 since the solubility of K_2TaF_7 is very low at room temperature. The precipitate is filtered, washed and dried. Niobium, tungsten, molybdenum, zirconium, uranium and thorium remain in solution. Repeated dissolution and precipitation may be useful in order to obtain extremely high purity tantalum. Elements such as niobium, tungsten, molybdenum, uranium and thorium, which are

30   difficult to remove by electron beam melting, are easily removed by this process.

Potassium heptafloutantalate can be reduced to tantalum metal by fused salt electrolysis or reduction by sodium. The rate of reduction by electrolysis is very slow, therefore sodium reduction is used for processing large quantities of K_2TaF_7 into tantalum metal. The overall reduction reaction can be written as

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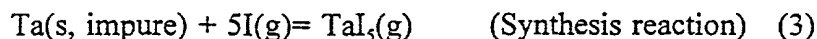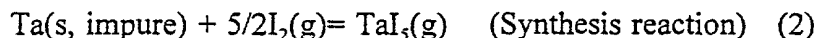1 $$K_2TaF_7 + 5Na(l) = Ta(s) + 2KF + 5NaF \quad (1)$$

Referring to the drawings, FIG. 1 shows a reduction furnace. The reduction is
carried out by placing K_2TaF_7 and some dilute salts such as KCl, NaCl, LiCl, CsCl, $CaCl_2$,
5   etc. into a reactor equipped with a stirring device. The reactor is placed in a furnace
heated to above the melting point of the salt mixture, usually under 1000°C. Molten
sodium is injected into the reactor and stirred while controlling the temperature. After
cooling, the mass is removed from the reactor, crushed and leached with a dilute acid to
recover tantalum metal powder. The powder is compacted and melted in an electron beam
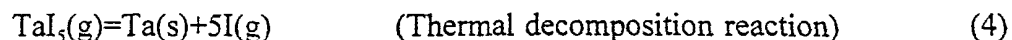10   furnace.

2) Iodide Process

Tantalum metal is produced from the reduction of commercially available K_2TaF_7
by sodium, which is a process similar to the Hunter process used for the production of
15   sponge titanium. The metal produced by the reduction of sodium contains most of the
impurities that exist in the K_2TaF_7 such as Fe, Ni, Ti, W, Mo, etc. The metal is in the
form of powder and has a very high oxygen content.

The method described herein is capable of producing high purity tantalum from
scrap or impure tantalum metal. The process is based on chemical transport reactions, in
20   which tantalum iodides are formed by the reaction of impure tantalum metal with iodine
gas (synthesis zone), at lower temperatures, then the tantalum iodides are decomposed on a
hot wire filament, at higher temperatures, to produce a very pure metal (deposition or
thermal decomposition zone.). The impure tantalum is converted into gaseous species
according to the following reactions in the synthesis zone:

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$$Ta(s, impure) + 5/2I_2(g) = TaI_5(g) \quad \text{(Synthesis reaction)} \quad (2)$$
$$Ta(s, impure) + 5I(g) = TaI_5(g) \quad \text{(Synthesis reaction)} \quad (3)$$

Similar reactions can be written for the other tantalum iodide species, such as TaI_3
30   and TaI_2. The gaseous species of tantalum diffuse into the thermal decomposition zone
and decompose to form pure tantalum metal according to the following reaction:

$$TaI_5(g) = Ta(s) + 5I(g) \quad \text{(Thermal decomposition reaction)} \quad (4)$$

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1   The thermodynamic factors are important to understanding and controlling the process. Thermodynamic calculations have been carried out to determine advantageous operating conditions. such as temperature and pressure. in the synthesis and decomposition zones.

5   A schematic diagram of the apparatus is shown in Figure 2. The process apparatus contains a cell, filament and feed material and is designed to run batch operations. After each run the apparatus is cooled to room temperature and disassembled.

The preferred iodide cell, for the refining of tantalum, is an alloy 600 (Inconel) container clad with a metal more electrochemically noble than tantalum according to the
10   chloride electromotive series, such as molybdenum or tungsten or an alloy thereof. The cladding prevents contamination of the refined tantalum by cell components since molybdenum and tungsten do not react with iodine at cell operating temperatures. Alloy 600 (Inconel) containers are also used for the refining of metals such as Ti and Zr, without cladding, since these metals are refined under different operating conditions.

15   A filament made of pure tantalum rod is used for the decomposition surface. The filament can be in the shape of a U or can be a different shape to increase its surface area. It is also possible to use multiple filaments to increase the surface area and cell productivity. The filament is heated resistively by an external power supply. Since the filament temperature affects the deposition rate, the current is controlled to maintain the
20   filament temperature between 1000 and 1500°C. Tantalum crystals then grow on the filament.

A cylindrical molybdenum screen is placed in the cell to provide an annular space 1 to 3 inches wide. The annular space if filled with tantalum feed material in the form of chips, chunks or small pellets. This type of arrangement gives a high surface area for the
25   reaction between feed material and iodine gas in the cell. The crude tantalum can also be compacted to a donut shape and placed in the reactor. The feed materials are cleaned with cleaning agents before they are charged into the cell.

A good vacuum system is advantageous to producing tantalum with low impurities. Therefore, the cell is connected to a vacuum system producing 1 micron or less of
30   pressure. The cell is evacuated at room temperature, then heated to around 800-1000°C under vacuum to remove all the volatile impurities before iodine is added.

The temperature in the synthesis zone effects the rate of reaction. The temperature in the synthesis zone should be uniform and kept much higher than boiling point of TaI_5. A special heater placed on the lid of the cell keeps the temperature at around 350-500°C,

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1   which prevents the condensation of iodides under the lid. Without this heater, iodine must be continuously added to the system.

Oxygen in tantalum originates from numerous sources, starting with the precursor and on through electron beam melting. Oxygen is undesirable at high concentrations due

5   to its effect on the resistivity of deposited tantalum thin films. Currently available methods cannot easily decrease the oxygen levels to less than 30 ppm. Thermodynamic calculations, as well as the experimental results, indicate that the metal oxides formed or present in the feed material do not react with iodine and are not transported to the decomposition zone. Therefore, this process is capable of producing high purity tantalum

10   with very low oxygen. The amount of oxygen remaining in the cell atmosphere is reduced by a combination of argon flushing and vacuum. Nitrogen in the feed material behaves like oxygen, therefore the nitrogen content of tantalum crystal bar will be very low.

Electron beam melting is frequently used to refine tantalum. However, electron-beam melting cannot remove elements such as tungsten and molybdenum, since the vapor

15   pressures of these elements are very low at the melting temperature of tantalum. The present process is capable of consistently removing elements such as tungsten and molybdenum to extremely low levels. The process may also remove uranium and thorium, which cannot be removed by electron beam melting.

The iodide process described above may not be able to remove significant amounts

20   of niobium. Therefore, the current process has been modified to obtain pure tantalum with very low metallic impurities including niobium. In the modified process, tantalum scrap or crude tantalum is reacted with iodine gas to form gaseous TaI_5 and NbI_5, which then are separated by fractional distillation, since the boiling points of these two compounds are different. A schematic of the apparatus is shown in Figure 3.

25   Crude tantalum or scrap is placed in a vertical tube made of Inconel and clad with molybdenum, tungsten or an alloy thereof. The tube is placed in a furnace that is heated to 400-700°C. A carrier gas such as clean argon or helium is passed over an iodine bath. The temperature of the bath is adjusted to get a specific I_2 partial pressure. Iodine gas reacts with tantalum scrap to produce gaseous tantalum and niobium iodide. The gas from

30   the feed reactor passes through the distillation columns. The temperature of the first column is maintained just below the boiling point of TaI_5, to condense TaI_5. The second column is maintained at a temperature low enough to condense NbI_5, but above the boiling point of I_2. The iodine gas is circulated through the process of reuse. All the gas lines between the first column and furnace are made of molybdenum and maintained at about

35   600°C, the others are maintained at lower temperatures.

1   The pure liquid or solid TaI_5 obtained from the fractional distillation unit is fed into the deposition rector and the TaI_5 decomposes on a hot surface to produce pure tantalum crystals. Tantalum obtained from this process is very pure and free of all impurities that cannot be removed by conventional processes. The pure tantalum obtained

5   by the modified iodide process is electron beam melted to produce high purity tantalum ingots.

3. Electron Beam Melting

Electron beam melting is commonly used to melt and refine refractory materials.

10   The process is based on the use of the intense heat generated when a high energy particle stream impinges on a material, transforming its kinetic energy into thermal energy. The flexibility to distribute energy yields a large number of electron beam melting techniques such as button, drip, hearth, zone melting, etc. for various metals. Electron beam hearth melting has been established for titanium and super alloys. Electron beam

15   drip melting may be used for refractory materials. An electron beam drip melting furnace compromises a horizontal bar feeder for primary feedstock. The bar feeder is equipped with a vacuum valve which allows nearly continuous feeding and melting of precompacted materials. The refining of refractory metals occurs via vaporization of suboxides, evolution and removal of gases, carbon-oxygen reaction and vaporization of metallic

20   impurities. Most of the elements can be removed from tantalum during melting by the one of above mechanisms. However, electron beam melting cannot remove W, Mo, Nb, U, Th, etc. due to low vapor pressures of these elements at the melting temperature. Repeated melting may be necessary to get very high purity materials.

Scrap, impure tantalum, tantalum powder obtained from electrolysis or reduction of

25   K_2TaF_7 is compacted and melted in an electron beam drip melting furnace to produce high purity tantalum ingots.

4. Target Manufacturing

Ingots obtained from electron beam melting are forged into billets and surface

30   machined. After surface machining, the forged billet is cut into pieces, which are further cold-rolled into blanks. The blanks are annealed in an inert atmosphere to obtain the desired microstructure. The blanks are then machined to obtain the final finish and may be bonded to copper or aluminum backing plates. A schematic of the target produced is shown in Figures 4A and 4B.

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1   It is desirable to perform a chemical analysis and characterization of targets by measuring the grain size and texture. The methods of chemical analysis useful to derive the chemical descriptions set forth herein are the methods known as glow discharge mass spectroscopy (GDMS) for metallic elements and LECO gas analyzer for non-metallic

5 elements. Line interception method is used for grain size determination and XRD and EBSP are used to obtain texture data.

EXAMPLE 1

    About 350 grams of K_2TaF_7 was added to 595 cc of HF (49%) in a Teflon beaker.

10 The mixture was heated to 90°C and stirred continuously. The beaker was covered with a Teflon plate to prevent evaporation of the solution. The dissolution process lasted about one hour. About 140 grams of KCl was dissolved in 700 cc of distilled water and heated to 60 C. The KCl solution was added to the K_2TaF_7 solution and the resulting solution was stirred for several minutes. The solution was cooled to room temperature which

15 caused the tantalum in the solution to be precipitated as K_2TaF_7, since the solubility of this compound is very low at room temperature. The precipitates were filtered and washed with KF solution (100 gr/liter H_2O) and distilled water. The powder was dried at 160°C in a vacuum furnace, then analyzed for composition. X-ray diffraction studies were carried out on the precipitates.

20   Several examples were carried out according the procedure described above and samples were analyzed. The niobium content of K_2TaF_7 was reduced by 50 percent after the first treatment. The results are shown in Table 1. The data shown in Table 1 indicates it is possible to decrease the niobium content of tantalum by this method. The purified K_2TaF_7 may be reduced by sodium.

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Table 1

Element	Original K_2TaF_7	K_2TaF_7 After First Wash	K_2TaF_7 After Second Wash
Nb	4.6	<2.2	<1
Mo	0.2	0.1	0.1
W	4.8	1.1	<1
Zr	0.52	0.14	<0.1
Th	<0.01	<0.01	<0.01
U	<0.01	<0.01	<0.01
Na	1100	130	50
Fe	4.8	1.2	<1
Al	2.5	1.2	
S	8.7	1.1	

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1   The data in Table 1 has shown that the contents of Nb, Mo and W are largely
lowered by this method. It is well known that these elements cannot be removed from Ta
metal by electron beam melting. Therefore, a removal of these three elements from the
K_2TaF_7 is beneficial to producing very pure tantalum. Assuming all Nb, Mo and W in the

5   K_2TaF_7 will be co-reduced with Ta in the sodium reduction stage and neglecting the
existence of all other elements listed in Table 1, a simple calculation can be made to show
the influence of the K_2TaF_7 purification on metal purity. A complete sodium reduction of
1000 g of original K_2TaF_7 would produce 461.7 g of Ta which would contain 9.6 mg of
Nb, Mo and W, resulting in a metal purity of 99.9979%. When using 1000 g twice washed

10   K_2TaF_7, 461.7 g of Ta produced by sodium reduction would contain less than 2.1 mg of
Nb, Mo and W. The metal purity would then be 99.9995%.

EXAMPLE 2

An iodide cell was used to produce pure tantalum from scrap available in the

15   market. The cell was made of an Inconel alloy and lined with molybdenum for the
preliminary experiments. A molybdenum screen was placed inside the cell and Ta scrap
was used to fill the gap between the screen and the cell wall. The cell was leak checked,
then evacuated to below 10 microns. The cell was heated to 850 C, under vacuum, to
evaporate and remove organic and other volatile compounds. Then the cell was cooled to

20   room temperature and the precipitates on the lid were cleaned. A filament made of pure Ta
was installed on the cell lid. The cell was sealed and evacuated to below 10 microns again.
The feed was heated to about 500-600°C and the filament to 1000-1200 C. When the feed
and filament temperature were stabilized, a measured quantity of iodine crystals were
added to the reaction chamber. The current and voltage supplied to the filament were

25   measured continuously. From these values it is possible to calculate the conductance,
which is related to the diameter of the bar. The vessel pressure, and filament and feed
material temperatures were controlled. Tantalum bars are successfully grown by this
method.

It was found that the temperature of the filament and feed as well as the pressure

30   affects the deposition rate significantly. The growth rate of Ta bar is related to
conductance of Ta bar. The growth rate in terms of conductance (Mho) is shown in Figure
5. Very high deposition rates are obtained by this method as shown in Figure 5. Chemical
analyses of the resulting tantalum bars from several runs are given in Table 2. It must be
noted that scrap used in the experiments was not homogenous in composition. The original

35   composition of the tantalum feed material is also shown in Table 2.

Table 2

		Run 1	Run 2		Run 3	Run 4
Time, hrs		79	45		62	45
Weight, gr		5925	5043		7829	5969

Element (ppm)	Feed 1 & 2	Run 1	Run 2	Feed 3 & 4	Run 3	Run 4
Nb	1200	900	505	90	185	230
Mo	6	1.2	1.7		1.3	1.2
W	30,000	0.28	0.19		0.2	0.25
O	100	90	308	100	60	176
N	100	<10	3	100	6	4

EXAMPLE 3

Tantalum crystal bars from various runs were melted in an electron beam furnace. The analytical results of the tantalum feed stock and the melted tantalum ingot are shown in Table 3.

Table 3

Element	Feed Material Concentration (Average ppm)	Concentration After Melting (Average ppm)
Fe	344	1
Ni	223	0.13
Cr	205	0.19
Nb	463	270
O	221	<25

EXAMPLE 4

Ingots obtained from electron beam melting are cold worked and annealed to produce target blanks. Initial ingot breakdown is done via a combinationof side and upset forging. After surface machining, the forged ingot is cut into pieces, which are further cold rolled into blanks. Two rolling temperatures are considered: room temperature and liquid nitrogen temperature. The former is called cold rolling, while the latter is referred to as cryogenic rolling. The reduction at rolling is in the range of 70 to 90%. The rolled blanks are annealed in an inert atmosphere or vacuum under different conditions to obtain the desired microstructure and texture.

1   EXAMPLE 5

Blanks with fine grains and desired texture are machined to obtain the final finish
and bonded to copper or aluminum backing plates. A schematic of the target produced is
shown in Figures 4A and 4B.

5   In the foregoing discussions, it is apparent that various changes and modifications
may be made within the preview of the invention. Accordingly, the scope of the invention
should be limited only by the appended claims.

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